A Discussion on Personnel Exposure to Posttest Byproducts from a 50-cal. Light Gas Gun

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Introduction

In January of 2002, employees working in the Hypervelocity Test Facility (HTF) at White Sands Test Facility (WSTF) began to notice common physical complaints. These included loss of smell, loss of taste, skin irritation, a burning sensation of the mucus membranes, and redness and chapping of the lips. These conditions extended to home during the weekends and throughout holiday breaks as well. Concerns about air contaminants were raised with regard to the operation of the .50-cal. two-stage light gas gun (2SLGG). Employees suspected that these conditions might be caused by air contaminants from small leaks at the gun pump tube joint at the breech, and exhaust gas entrainment into the HVAC systems. The WSTF Industrial Hygienist (IH) was notified and samples were collected using the MIRAN infrared spectrometer (real time) air sampler on 08 January 2002 at the .50-cal. gun. The results from this screening test suggested the need for more detailed investigations with analytical sampling and analysis.

Background

In 1994, bulk posttest air samples were collected from the then new 1-in. 2SLGG. Bulk air samples were collected from the pump tube and analyzed by gas chromatography (GC) with a flame ionization detector (FID) and GC with a mass selective detector (MSD). The results revealed the presence of several gases with concentrations that were above OSHA control levels. These gases were acetaldehyde, ammonia, benzene, carbon dioxide, carbon monoxide, hydrogen cyanide, and methylaniline. Dose data were not obtained. A requirement for a 1-h gaseous nitrogen (GN_2) purge was established after it was shown that a 45-min purge would reduce the pump tube concentration of these gases to only a fraction of control levels.

When the extensively used .50-cal. gun was installed in WSTF Building 272 in 1998, an identical 1-h GN_2 purge was adopted based on the assumption that it was acceptable for the smaller volume of the .50-cal. gun. However, in 2001-02, it was not working properly and personnel were feeling the effects. An investigation ensued and several items were found to

be contributing to the release of post-shot gases. First, the pump tube end that mates with the breech was found to have small longitudinal gouges. These gouges prevented the O-ring from sealing the joint. Second, the purge lines were filled with soot from the shots. The lines remained connected during shots to pull vacuum, deliver hydrogen, and purge the pump tube. The pressure of the expanding gun powder gases was forcing debris into the ¼-in. line, which reduced the flow to a crawl; but the pressure gauges used to set the purge pressure read correctly. Third, the 50-cal. gun was positioned on the west, or windward, side of the building, which is the direction of the prevailing winds in Las Cruces. This position was contributing to the entrainment of gases into the HVAC systems. (The 1-in. gun is on the leeward side of the building.) Fourth, the overpressure relief devices on the flight ranges emptied directly into the gun lab. When the pump tube gases leaked past the piston they soon entered the breathing-air zone. Corrective actions have improved but not completely alleviated these conditions.

WSTF HTF Ignition Materials

The ignition chain used in WSTF's 50-cal. LGG include igniters that contain two sizes of black powder, an ignition compound, and the propellants used to accelerate the piston. Attachment A contains the material safety data sheet (MSDS) that provides more details. The propellant is typical extruded tubular IMR 4198 single-based nitrocellulose powder, available at most sporting goods stores in America.

The materials used to build the exoskeleton of the powder cone are double-sided 3M® [1] tape, brown construction paper, masking tape, and cotton. Downstream of the breech there is an acrylic disk and a high-density polyethylene piston. Residue remaining from the gun cleaning process is typically isopropyl alcohol.

Sampling and Analysis

The first sampling occurred on 08 January 2002. It was performed with the help of the IH present using the MIRAN air sampler. The WSTF MIRAN uses infrared (IR) spectrometry. It is good at recognizing groups of compounds but has trouble distinguishing between individual chemicals. At this point, no personnel protective measures were used. The MIRAN results with 175-grams of 4198 gunpowder are shown in Table 1. Figure 1, a schematic of the 2SLGG, identifies the sampling locations.

The data revealed alarming amounts of benzene, acetaldehyde and ammonia. All testing was suspended pending further investigation.

[1] 3M® is a registered trademark of Minnesota Mining and Minerals Co., St. Paul, Minnesota.

Table 1
MIRAN Preliminary Results

Sample	Location	Sequence in Operation	Max. Reading for Benzene[a] (ppm)	Max. Reading for Acetaldehyde (ppm)	Max. Reading for Ammonia (ppm)
1	Breech	After gun is fired but prior to purges	13	8.3	0.7
2	High-pressure section	After gun is fired but prior to purges	4.7	6.2	6.8
3	Break area (table)	After gun is fired but prior to purges	3.9	3.8	NR[b]
4	Target chamber open	After 15 min purge, evacuation and backfill with ambient air	3.2 (outside)	11 (inside)	3.9 (outside) 2.6 (inside)
5	Expansion tank open	After 15 min purge, evacuation and backfill with ambient air	2.8 (outside) 6.4 (inside)	NR	1.4 (inside)
6	Disconnected breech from pump tube	Purged pump tube for 1 h. Gun is opened.	22	NR	NR
7	Disconnected high pressure section from pump tube	Purged pump tube for 1 h. Gun is opened.	66	NR	NR
8	Break area	After purge, gun is opened, N. high-bay door opened and fans turned on for ~ 3 min.	3	NR	NR

[a] Short Term Exposure Limit is 2.5 ppm
[b] No reading was taken with the MIRAN
NOTES: No hydrogen cyanide was detected.
Highest level of CO detected was 1 ppm. Highest level of CO_2 detected was 644 ppm.
The MIRAN samples a spectrum and may not distinguish between specific gases.

On 17 January 2002, in order to analyze the posttest chemicals more precisely, WSTF performed a 50-cal. hypervelocity test with a gunpowder load of 225 grams of IMR 4198 and collected samples. This test was performed with a WSTF-supplied aluminum target and projectile. The objective of this test was to obtain air quality samples and not hypervelocity test data.

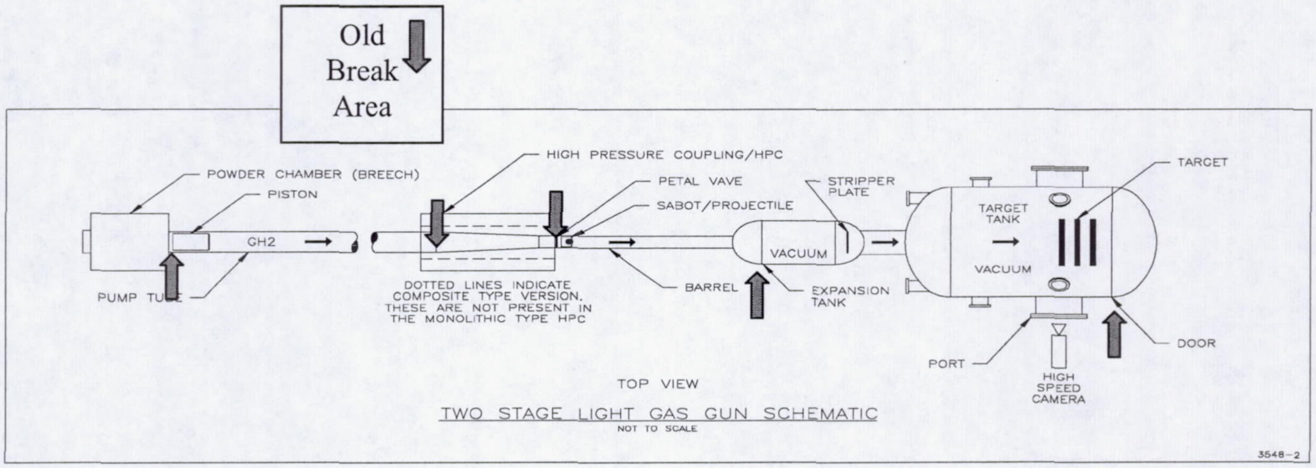


Figure 1

Schematic of 2SLGG

Red arrows indicate sampling locations.

NOTE: The flight range is defined as everything to the right of the petal valve.

For this shot, three different methods of sampling were planned. Wipe, soot, and gas samples were collected at various points along the gun (Figure 1). To totally protect personnel from exposure to suspected chemical contaminants, self-contained breathing apparatus (SCBA), Tyvek® [2] suits and taped latex gloves were worn during posttest operations and sampling.

Wipe Sampling

The IH and hypervelocity personnel collected wipe samples from the locations shown in the sampling matrix (Table 2). The WSTF Chemistry and Metallurgical Laboratory (Chem Lab)

Table 2

Sampling Matrix for Hypervelocity Wipe Samples

Location	Sampled Area (ft^2)	Date
Pump tube breech	1	06 February 2002
Flight range expansion tank	1	06 February 2002
Flight range target chamber	1	06 February 2002
Blank	N/A	06 February 2002
Back of piston	0.11	06 February 2002
Breakroom table	1	18 January 2002
Rail	1	18 January 2002
Work bench	1	18 January 2002
Blank	N/A	18 January 2002

[2] Tyvek® and Teflon® are registered trademarks of E. I. du Pont de Nemours and Company, Wilmington, Delaware.

provided 10 μm Teflon®[2] membrane filters (Millipore®[3] part # LCWP 047 00) in clean glass screw-cap bottles. A 1-ft^2 area was sampled where possible. After wiping the designated area with the filter, the filter was immediately returned to the sample bottle and delivered to the analytical group of the Chem Lab for analysis. 2 mL of dichloromethane were added to the sample bottles containing the filters. The bottles were then sonicated for 5 min. Aliquots of the dichloromethane were removed and filtered through 0.45-μm syringe filters. 1 μL of each sample was analyzed by GC/MSD.

Wipe Results:

The results from the wipe samples taken from the pump tube breech are shown in Table 3. The method detection limit for the pump tube breech sample is 0.1 ng/ft^2. The results from the wipe samples taken from the back of the piston are also shown in Table 3. The method detection limit for the back-of-piston sample is 0.9 ng/ft^2. No compounds above the reporting limit (0.1 ng/ ft^2) were detected in the flight range expansion tank sample or the flight range target chamber sample.

A solid identified in wipe samples was 2-methyl-1,3-benzenediamine. It is a potent skin sensitizer and irritant. Post-shot residue on the skin creates a tangible sensation. Some animal tests have indicated it is a possible carcinogen; however, other tests have failed to show that this compound is carcinogenic.

Soot Sampling

Two duplicate soot samples from the Building 272 target chamber were collected by hypervelocity personnel and analyzed by the analytical group of the Chem Lab. 10 mL of dichloromethane were added to the sample bottles containing the filters. The bottles were then sonicated for 5 min. Aliquots of the dichloromethane were removed and filtered through 0.45-μm syringe filters. One μL of each sample was analyzed by GC/MSD.

Table 3
Wipe Sample Results

Compound	Retention Time (min)
Pump Tube at Breech	
Octamethylcyclotetra-siloxane	5.79
Decamethylcyclopenta-siloxane	7.01
Unknown compound	8.33
2-methyl-1,3-benzenediamine	8.69
Tetradecamethylcyclohepta-siloxane	9.51
Hexadecamethylcycloocta-siloxane	10.56
Back of Piston	
Decamethylcyclopenta-siloxane	7.01
Dodecamethylcyclohexa-siloxane	8.32

[3] Millipore® is a registered trademark of Millipore Corp., Bedford, Massachusetts.

Soot Results:

Organic based compounds were found in insufficient quantities to identify.

Air Sampling

Certified, evacuated offgassing containers were used to collect air samples at various locations. Each offgassing container has a nominal internal volume of 4.3 liters. Table 4 shows the location and sampling times for each sample collected (Figure 1). The air samples were transported to the Molecular Desorption and Analysis Laboratory (MDAL) for analysis. The samples were analyzed by GC with FID and by GC with a dual infrared detector (IRD) and MSD. For the analysis, a list of target compounds was specified. The target compounds were benzene, ammonia, acetaldehyde, methanol, and ethylene. Additionally, all observed compounds were determined to the lowest level possible.

Air Sampling Results:

Table 5 shows the results of the pre- and post-purge air sampling.

Table 4
Sampling Matrix for .50-Cal Gun Air Samples

Location	Time & Date of Sampling	Pressure (psia ± 2%)
Baseline	0817 hrs 17 January, 2002	12.60
Breech posttest	0910 hrs 21 February, 2002	12.46
#2 High-pressure post	0915 hrs 21 February, 2002	12.56
#5 Pump tube pre-purge	0920 hrs 21 February,2002	10.81
#6 Inside target chamber	1036 hrs 21, February, 2002	12.57
#7 Inside expansion chamber	1042 hrs 21 February, 2002	12.62
#11 Breech post-purge	1124 hrs 21 February, 2002	12.65
#13 High-pressure post-purge	1113 hrs 21 February, 2002	12.63
Flight range	1045 hrs 06 February,2002	12.49
Breech	1155 hrs 22, February, 2002	12.59
High-pressure accelerator reservoir	1203 hrs 22, February, 2002	12.45

Table 5

Pre- and Post-Purge Air Sampling Results

Compound	Chemical Abstracts Service* (CAS) Number	Pre-Purge Quantity	Post-Purge Quantity	Time Weighted Average (TWA)	Immediate Danger to Life or Health (IDLH)
		(ppm)			
Methane	74-82-8	1200	54	1000	
Carbon monoxide	630-08-0	>>8500[a]	13	25	1200
Ammonia	7664-41-7	28 - 182	5.5	25	300
Hydrogen sulfide	353-50-4	NA	ND	10	100
Carbonyl sulfide	7783-06-4	140	0.08	NA	500
Propane	74-98-6	16	0.09	1000	2100
Propylene	115-07-1	120	.7	Asphyxiant	400
Propyne	74-99-7	5.7	.03	NA	
Hydrogen cyanide	74-90-8	260	ND	4.7 C	50
Isobutane	75-28-5	2.0	ND	800	
Acetaldehyde	75-07-0	4.9	0.23	25 C	2000
Unidentified component	--	9.9	ND	NA	
Methyl alcohol	67-56-1	13	0.43	NA	6000
Butene	106-98-9	29	0.24	NA	
1,3-Butadiene	106-99-0	28	.22	5 C	2000
Butane	67-56-1	1.2	ND	1000	
Butenes	--	47	0.11	NA	
2-Butyne	503-17-3	0.50	ND	NA	
Methyl mercaptan (Methanethiol)	106-97-8	11	ND	100 C	150
C5-C12 Saturated and unsaturated aliphatic hydrocarbons	--	93	ND	1000	
Acetonitrile	75-05-8	22	0.26	20	500
Acetone	67-64-1	12	0.16	500	2500
1-Pentene	109-67-1	2.0	ND	600	1500
Furan	110-00-9	0.29	ND	NA	
Isopropyl alcohol	67-63-0	2.4	0.25	NA	2000
Acrylonitrile	107-13-1	0.83	ND	2	85
Carbon disulfide	75-15-0	1.2	ND	10	500
Propane nitrile	107-12-0	2.5	ND	NA	
Cyclopentene	142-29-0	1.9	ND	600	750
Unidentified component	--	0.15	ND	NA	
Butyraldehyde	123-72-8	0.39	ND	NA	
Methyl ethyl ketone	78-93-3	1.9	ND	200	3000
Unidentified component	--	0.30	ND	NA	
Hexene	592-41-6	5.2	ND	50	
Methyl acrylate	96-33-3	2.1	ND	2	250
Unidentified component	--	0.08	ND	NA	
n-Butyl alcohol	71-36-3	9.3	0.11	NA	1400
Benzene	71-43-2	74	0.01	0.5	500
Thiophene	110-02-1	0.40	ND	NA	
Methyl isobutyrate	547-63-7	0.15	ND	NA	
2-Pentanone	107-87-9	0.08	ND	NA	1500
Methyl methacrylate	80-62-6	19	0.10	50	1000
Unidentified component	--	0.28	ND	NA	
Heptene	80-62-6	1.6	ND	NA	
Unidentified component	--	2.7	ND	NA	
Unidentified component	--	0.27	ND	NA	
Toluene	108-88-3	23	0.33	50	500
Unidentified component	--	0.40	ND	NA	
Octene	111-66-0	0.54	ND	NA	
Octane	111-65-9	0.21	ND	300	1000

Compound	Chemical Abstracts Service* (CAS) Number	Pre-Purge Quantity	Post-Purge Quantity	Time Weighted Average (TWA)	Immediate Danger to Life or Health (IDLH)
		(ppm)			
Hexamethylcyclotrisiloxane	541-05-9	8.1	0.29	NA	
Vinylcyclohexene	100-40-3	0.16	ND	0.1	
Ethylbenzene	100-41-4	1.8	0.05	100	
Xylenes	--	10	0.12	100	900
Styrene	100-42-5	1.4	0.22	20	700
Nonene	124-11-8	0.19	ND	200	
Unidentified component	--	0.17	ND	NA	
Isopropyl cyclohexane	696-29-7	0.41	ND	NA	1300
C9-C10 Aromatic hydrocarbons	--	4.6	ND	1000	
Propyl benzene	103-65-1	0.20	ND	NA	
Methyl stryene	98-83-9	0.31	ND	50	700
C7 Unsaturated alcohol	--	0.40	ND	NA	
Octamethylcyclotetra-siloxane	556-67-2	3.7	0.25	NA	
Benzonitrile	100-47-0	0.31	ND	NA	
Decene	--	1.2	ND	NA	
Unidentified component	--	6.7	ND	NA	
C8 Alcohol	--	1.2	ND	NA	
3-Phenyl-propene	300-57-2	0.39	0.01	NA	
Limonene	5989-27-5	0.74	0.03	NA	
Indane	496-11-7	0.33	ND	NA	
Indene	95-13-6	3.4	0.07	10	
Unidentified nitrogen containing component	--	2.1	ND	NA	
Unidentified component	--	5.9	0.43	NA	
Decamethylcyclopenta-siloxane	541-02-6	0.76	0.02	NA	
Naphthalene	91-20-3	3.3	0.02	10	250
Methyl naphthalenes	--	0.31	ND	NA	

NA = Not Available ND = None Detected C = Ceiling Limit (not to exceed)

* Chemical Abstracts Service (CAS) is a division of the American Chemical Society

[a] The chemical analysis for this sample yielded a result that only allows the concentration to be calculated as >> 8500 ppm. A concentration of 36000 ppm can be projected using the methane and carbon monoxide concentrations from sample 02-36469G, assuming comparable proportions.

Discussion

The data in the pump tube pre-purge show there were a large number of chemical compounds identified prior to purging. Notably, many of the quantities are near or above the established control limits of the Center for Disease Control, OSHA, NIOSH and ACGIH. Several of the compounds are considered carcinogens by these regulatory agencies. Others compounds, such as acetaldehyde, ethyl benzene, and methyl ethyl ketone, are on the "further study list" of chemical substances and other issues under study by the TLV Chemical Substances Committee. Solicitation for additional information continues on these chemicals because they are confirmed animal carcinogens and their biological effects in humans are not adequately understood. There is not yet enough toxicological information to definitively implicate them to a more severe threshold limit value (TLV) category.

Another important point is that TLVs are developed for single chemical substances. As you can see, the pump tube environment is comprised of a complex composite of chemicals. There are several possible modes of chemical mixture interaction. Additivity occurs when the combined biological effect of the components is equal to the sum of each of the agents given alone. Synergy occurs when the combined effect is greater than the sum of each agent. This is particularly serious when two or more hazardous substances have similar toxicological effects on the same organ or system. The situation is further complicated when solvents such as acetone, butyl acetate and methyl ethyl ketone, to name a few from Table 5, are combined with carcinogens such as benzene, acrylonitrile and 1,3-butadiene, to name a few others from Table 5. Solvent and carcinogen combinations make the carcinogens more readily absorbed, which lowers the control limits. It is likely that all three mixture interactions are going on here.

Table 5 also proves the importance of a proper 1-h pump tube purge. Most of the compounds were reduced to a none-detected (ND) level. The remaining compounds are well below control limits.

In the target tanks, the most prominent chemicals found were carbon monoxide, hydrogen and phthalates. Phthalates are used primarily as plasticizers and are usually added in proprietary amounts, but are known to be mucous membrane sensitizers.

Controls Used at WSTF

The hypervelocity team continues to identify design improvements and implement operational deviations to reduce or eliminate the risk of exposure to personnel. These improvements are maintained on all existing indoor gun systems and are included in the design of new gun systems and operational procedures. A list of engineering/design and procedural requirements, with discussion, is provided as follows:

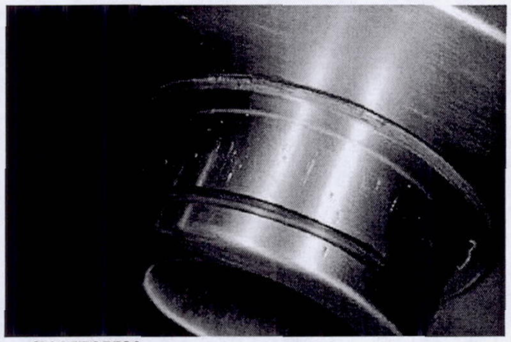
1. Exhaust vents on all indoor vacuum pumps were captured and routed outside to a minimum height of 3 ft above the roofline. This effluent was originally excreted into the room but is now captured.
2. Fresh air dump valves were installed on all flight ranges. This fresh air exchange is to be performed a minimum of four times. An analysis of evacuated chambers indicates a cycle of four fresh air dumps and subsequent evacuations provides a thorough exchange that removes potentially toxic substances and replaces them with high-quality air.
3. Polycarbonate lift-off plates were installed on all indoor flight ranges and, when possible, opposite the GN_2 purge fill line. The exhaust is captured and vented outdoors above the roofline. The lift-off plates serve three purposes. First, there is a small risk of over-pressurizing flight ranges during the test process. The lift-off plate thusly serves as a captured relief valve for the flight range. Second, a GN_2 purge is required after each test to evacuate gases and particulate. The GN_2 purge flow is controlled to lift off the plate and provide a captured path for this purge. Since the plate can be viewed lifting, one can check the flow. Third, the polycarbonate is translucent, which provides a place to use photo diodes to capture muzzle exit times.

4. Flow indicators were installed on the input side of the pump tube GN_2 purge lines on the 1-in. and .50-cal. guns. These help ensure that a proper GN_2 flow is achieved and maintained throughout the purge cycle. The pump tubes are quite dirty and contain high-pressure gases on the large guns, which can plug the fill lines. There is a history of these lines clogging with debris and choking off the purge gas flow.
5. Exhaust fans are used during testing to help evacuate gases.
6. Pump tube O-rings are inspected and usually replaced after each shot. It was found that in cleaning the mating sections of the pump tube, O-rings were scoured and, therefore, not providing a proper seal.
7. Ridge vents are closed immediately after the shot but before the purge cycles begin. This helps to keep exhaust gases from entering the building.
8. Personnel don appropriately selected negative pressure respirators with MSA GME P-100 cartridges when exiting the bunkers, safing, and inspecting the guns.
9. Two SCBA units, Tyvex suits, and latex gloves are located in the instrumentation bunker during all large caliber tests. Donning this equipment is required if there is a known leak during the test and, therefore, a potentially hazardous environment existing around the gun.
10. MSA Passports, capable of monitoring for multiple gases at once, are used during testing and placed near the pump tube and breech during the purge cycles. They currently monitor for CO, LEL and oxygen level. CO is used as an indicator gas. If CO levels are high, it is assumed that the levels of benzene, acetylaldahyde, and hydrogen cyanide are also high. If the CO warning alarm sounds, personnel are instructed to evacuate the area.

Work to completely eliminate the problem is still ongoing. Recently, the summer-storm winds forced air into the fresh-air ventilation system. Measures are underway to eliminate this problem. We also recently purchased an overhead vehicle exhaust system, which we can place directly over the breech during testing and cleaning operations.

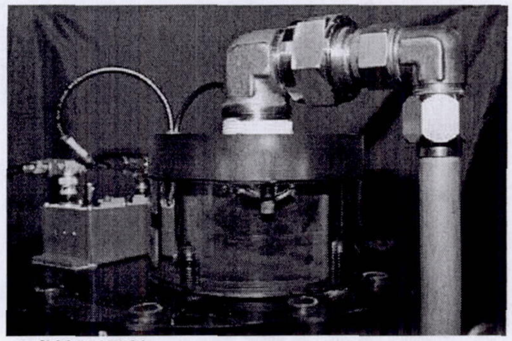
Conclusions

Sampling and analysis indicate that workers can quickly be overexposed to a hazardous composite of chemicals if pump tube purges are not performed, are performed inadequately, or if entrainment of exhaust into HVAC systems occurs. Air samples taken on the pump tube of a .50-cal. 2SLGG prior to a GN_2 1-h purge indicate that hazardous chemical mixes, including several known and suspected carcinogens combined with solvents, exist in quantities large enough to overexpose workers and support personnel. Please keep in mind that these samples were taken after tests with only 225 grams of powder. Since this is a relatively small amount of gunpowder when compared to larger 2SLGGs, it is imperative that facilities set up purging systems to evacuate the hazards. Measures must be taken to prevent exposing personnel to this dangerous mixture. Post-purge analysis indicates that all substances are reduced well below the control limits, although it is wise to consider that pockets of trapped gases may still occur.



wstf0905E07780

Pump Tube End



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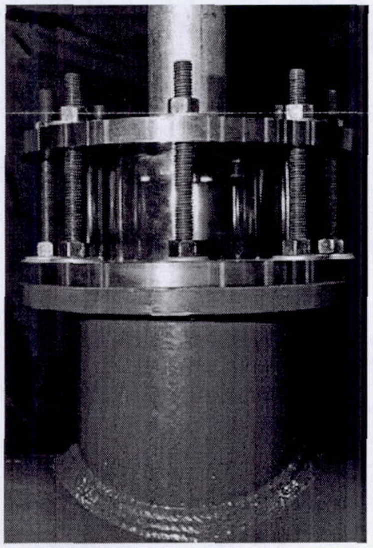
Capture Vent



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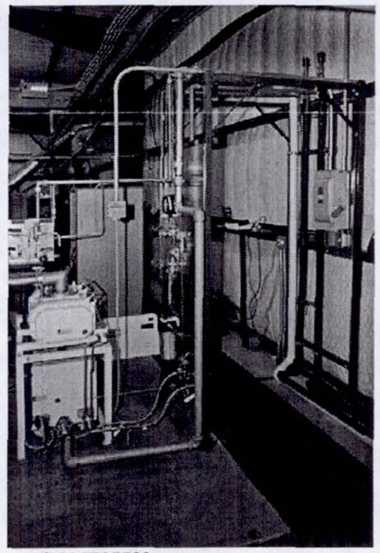
Capture Vent2



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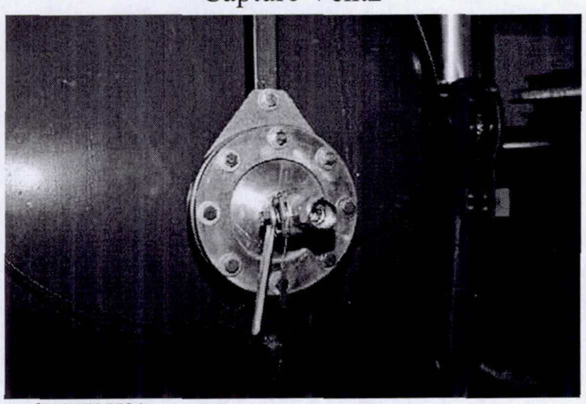
Vacuum Pump Vent



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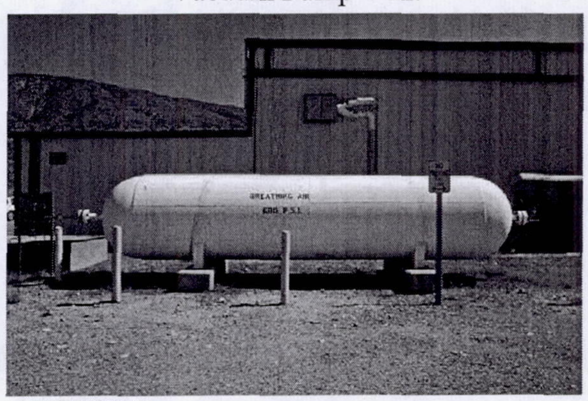
Fresh Air Valve



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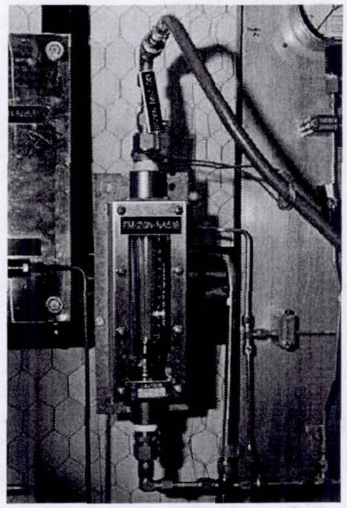
Air Tank



wstf0905E07786
Flow Meter

Recommendations

To reduce exposure to hazardous airborne substances and soot particulate, the following recommendations are offered:

1. Install a forced purge system from one end of the pump tube to the other. Monitor the flow through the tubing, as particulate may eventually plug the purge lines, preventing an inadequate purge.
2. Run purge lines outside and several feet above the roofline and away from HVAC intake louvers. (Design recommendations are available from the WSTF HTF.)
3. Purge the flight ranges in a similar fashion to the pump tubes, but with less pressure.
4. Pull vacuum on the flight ranges, and backfill with fresh and clean ambient air more than four times to remove all contaminants.
5. Use captured lift-off type vent valves on the flight range.
6. Overhead ventilation and source ventilation are recommended and should be turned on prior to firing the gun.
7. Increase the air exchange in the lab as much as possible. The WSTF building uses two high-volume exhaust fans, ridge vents, and three 10,000-CFM evaporative coolers.
8. Source exhaust systems, such as welding or vehicle exhaust hoods, work very well, especially during winter.
9. Consider bagging the connective joints so that if there is a leak, it is indicated by a puffed-up or torn bag.
10. If purging is not possible, it is suggested that SCBA units be used or, at a minimum, full facemask respirators with GME P-100 filter cartridges to protect personnel during posttest operations.

11. In case of a failure and resulting large release of gases, it is recommended that personnel maintain SCBA gear in a safely accessible location.
12. Oilless vacuum pumps prevent contaminants from impregnating the vacuum pump oil. The oil is considered a hazardous waste once contaminated and should be incinerated.
13. Workers should wear latex gloves, coveralls, and eye protection when cleaning the pump tube.
14. Cleaning rags and fluids must be collected and disposed of properly in order to prevent further contamination of personnel or the environment.
15. Non-essential personnel visits to the area should be kept at a minimum until the pump tubes are purged and cleaned.
16. Design exhaust stacks according industry ventilation standards. (Design recommendations are available from the WSTF HTF.)
17. A cost-effective means of monitoring the air quality in a lab is to purchase a carbon monoxide detector. It is used as an indicator gas: If it is present in high quantities, then you can assume all the other toxins are present.

References

American Conference of Governmental Industrial Hygienists (ACGIH), *Pocket Guide of TLVs and BEIs for Chemical Substances and Physical Agents and Biological Exposure Indices,* www.acgih.org

Center for Disease Control (CDC) - National Institute for Occupational Safety and Health (NIOSH), http://www.cdc.gov/niosh, and *NIOSH Pocket Guide to Chemical Hazards (NPG) - Index of Chemical Names and Synonyms*, latest revision.

CFR Title 29. *Labor*. Part 1910, *Occupational Health and Safety Standards.* Subpart Z, Toxic and Hazardous Substances, Code of Federal Regulations, http://www.osha.gov

Attachment A
MSDSs

IMR 4831

IMR

IMR POWDER COMPANY

RD No. 5, Box 247E, Plattsburgh, N.Y. 12901 – Tel: (XXXXXXXXXXXX

MATERIAL SAFETY DATA SHEET

PRODUCT IDENTIFICATION

NAME: SINGLE BASE SMOKELESS POWDER
TRADE NAMES AND SYNONYMS:

IMR-####, SR-####, PB

= Number Designation for Products

MANUFACTURER

PRODUCT INFORMATION PHONE:
MEDICAL EMERGENCY PHONE:
TRANSPORTATION EMERGENCY PHONE: (514) 371-5520

HAZARDOUS COMPONENTS

CHEMICAL	CAS NUMBER
Nitrocellulose	9004-70-0
2, 4-Dinitrotoluene	121-14-2

PHYSICAL DATA

Specific Gravity: 1.65
Solubility in H_20: Negligible
Color: Black
Form: Perforated or nonperforated small discs or perforated cylinders.

HAZARDOUS REACTIVITY

INSTABILITY: Unstable with heat, Unstable with static charges. Unstable with impact. Not hazardous if product used properly.
INCOMPATIBILITY: Incompatible with acids, alkalies, oxidants.
DECOMPOSITION: Decomposes with heat. Hazardous gases produced are carbon monoxide. Decomposes with impact, static charges.
POLYMERIZATION: Polymerization will not occur.

The data in this Material Safety Data Sheet relates only in the specific material designated herein and does not relate to use in composition with any other material or in any process.

Material Safety Data Sheet
May be used to comply with
OSHA's Hazard Communication Standard,
29 CFR 1910.1200. Standard must be
consulted for specific requirements.

Igniter

U.S. Department of Labor
Occupational Safety and Health Administration
(Non-Mandatory Form)
Form Approved
OMB No. 1218-0072

ITY (As Used on Label and List)

Note: Blank spaces are not permitted. If any item is not applicable, or no information is available, the space must be marked to indicate that.

Section I

Manufacturer's Name QTK, INCORPORATED	Emergency Telephone Number 1-877-368-5505
Address (Number, Street, City, State, and ZIP Code) P.O. BOX 744	Telephone Number for Information (605) 662-5171
COUNTY ROAD 6E	Date Prepared 28 AUGUST 2000
EDGEMONT, SD 57735	Signature of Preparer (optional)

Section II — Hazardous Ingredients/Identity Information

Hazardous Components (Specific Chemical Identity; Common Name(s))	OSHA PEL	ACGIH TLV	Other Limits Recommended	% (optional)

ITEM: Hypervelocity Free Flight Facility Igniter, Electrically Initiated.
Drawing: NASA - A337 - 6202 - M26 Rev. B
EX - 0009065
UN - 0276

HAZARDOUS INGREDIENTS: Primer Mix 487 - Approximately 100 mg. contained in unit
Black Powder - Approximately 9 gms., spillable if unit is ruptured, or crushed. See Sec. IV

Section III — Physical/Chemical Characteristics

Boiling Point	N/A	Specific Gravity (H_2O = 1)	Black Powder	1.70-1.82
Vapor Pressure (mm Hg.)	N/A	Melting Point		N/A
Vapor Density (AIR = 1)	N/A	Evaporation Rate (Butyl Acetate = 1)		N/A

Solubility in Water
Black Powder, Good. Primer Mix 487, Good.

Appearance and Odor
Black, Granular

Section IV — Fire and Explosion Hazard Data

Flash Point (Method Used)	Flammable Limits	LEL	UEL
N/A		392°F	867°F

Extinguishing Media
Water

Special Fire Fighting Procedures
Do not fight explosives fires

Unusual Fire and Explosion Hazards
When ignited unconfined, it burns with explosive violence and will explode if ignited under even slight confinement.

(Reproduce locally)

OSHA 174, Sept. 1985

Section V — Reactivity Data

Stability			Conditions to Avoid
	Unstable	X	Keep away from heat, sparks and open flame. Avoid impact,
	Stable		friction and static electricity.

Incompatibility (*Materials to Avoid*)
None

Hazardous Decomposition or Byproducts
Detonation produces hazardous overpressures. Gases may be toxic if in an area with inadequate ventilation.

Hazardous Polymerization			Conditions to Avoid
	May Occur		
	Will Not Occur	X	

Section VI — Health Hazard Data

Route(s) of Entry: Inhalation? Skin? Ingestion?

Health Hazards (*Acute and Chronic*)

Carcinogenicity: NTP? IARC Monographs? OSHA Regulated?
None of the components of black powder are listed as carcinogen.

Signs and Symptoms of Exposure
A detonation may cause severe injury.

Medical Conditions
Generally Aggravated by Exposure

Emergency and First Aid Procedures
Seek prompt medical attention.

Section VII — Precautions for Safe Handling and Use

Steps to Be Taken in Case Material Is Released or Spilled
Remove sources of friction, impact, heat, low level electrical current, electrostatic and RF energy.

Waste Disposal Method
Desensitize by deluting in water, or open train burn by qualified personnel.

Precautions to Be Taken in Handling and Storing
Store loaded items in cool, dry, approved magazine.

Other Precautions
Wear required protective clothing and grounding equipment when handling explosive devices.

Section VIII — Control Measures

Respiratory Protection (*Specify Type*)
None

Ventilation			
Local Exhaust		Special	
Mechanical (*General*)		Other	Adequate ventilation

Protective Gloves: None required
Eye Protection: Always when handling explosive devices

Other Protective Clothing or Equipment
Metal-free and non-static producing clothes.

Work/Hygienic Practices
Always keep work areas clean.

* U.S.G.P.O.: 1986-491-529/45775

IMR 4831

IMR

IMR POWDER COMPANY

RD No. 5, Box 247E, Plattsburgh, N.Y. 12901 – Tel: (6XXXXXXXXXX

MATERIAL SAFETY DATA SHEET

PRODUCT IDENTIFICATION

NAME: SINGLE BASE SMOKELESS POWDER
TRADE NAMES AND SYNONYMS:

IMR-####, SR-####, PB

= Number Designation for Products

MANUFACTURER

PRODUCT INFORMATION PHONE:
MEDICAL EMERGENCY PHONE:
TRANSPORTATION EMERGENCY PHONE: (514) 371-5520

****

HAZARDOUS COMPONENTS

CHEMICAL	CAS NUMBER
Nitrocellulose	9004-70-0
2, 4-Dinitrotoluene	121-14-2

****

PHYSICAL DATA

Specific Gravity: 1.65
Solubility in H_2O: Negligible

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HAZARDOUS REACTIVITY

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POLYMERIZATION: Polymerization will not occur.

The data in this Material Safety Data Sheet relates only in the specific material designated herein and does not relate to use in composition with any other material or in any process.

FIRE AND EXPLOSION DATA

Ignition Temperature: 160-170 degC

FIRE AND EXPLOSION HAZARDS

Hazardous gases produced in fire are carbon monoxide. Class B Explosive(DOT)>100lbs;Flammable Solid 100 lbs or less. Burns uncontrollably. Produces shrapnel if confined.

EXTINGUISHING MEDIA

None.

SPECIAL FIRE FIGHTING INSTRUCTIONS

Do not fight fire. Isolate area. Evacuate personnel to a safe area. Guard against intruders.

****

HEALTH HAZARD INFORMATION

INCIPAL HEALTH HAZARDS

These products have not been tested for toxicity. They are Class B Explosives and burning, confined or unconfined, can cause physical injury, including death. The toxicity effects given below for the hazardous components may result from gross chronic or acute overexposure to the products by inhalation, eye or skin contact or ingestion.

2,4-DINITROTOLUENE
Inhalation LC50: 2.87 mg/l, 1 hour in rats.
Skin Absorption ALD: >1,000 mg/kg in rabbits.
Oral LD50: 177 mg/kg in rats.

This compound is toxic by inhalation and ingestion. It is a skin and eye irritant. Toxic effects described in animals from exposure by inhalation, ingestion, or skin contact include nonspecific effects such as reduced weight gain, methemoglobinemia and effects on the central nervous system, the reproductive system, and bone marrow. In animal tests, technical grade 2,4-dinitrotoluene has carcinogenic activity. Tests for mutagenic activity in bacterial and mammalian cell cultures have been both positive and negative. It has demonstrated no embryotoxic activity in animals. It produces testicular degeneration and decreased spermatogenisis in rats, mice and dogs. Reduction in male fertility occurs in dominant lethal studies in rats.

Human health effects from overexposure by inhalation, skin or eye contact or ingestion may initially include reduction of the blood's oxygen carrying capacity with cyanosis, weakness, or shortness of breath by methemoglobin formation; nonspecific discomfort such as nausea, headache, confusion.

IMR

IMR POWDER COMPANY

RD No. 5, Box 247E, Plattsburgh, N.Y. 12901

irritation effects with cough, discomfort, difficulty breathing, or shortness of breath; or joint pain. The compound appears to be able to significantly permeate the skin. Individuals with preexisting diseases of the central nervous system, peripheral nervous system, lungs, or reproductive organs may have increased susceptibility to the toxicity of excessive exposures.

NITROCELLULOSE
Oral LD50: >5,000 mg/kg in rats.

The compound is not a skin or eye irritant.

CARCINOGENICITY
NONE OF THE COMPONENT(S) OF THIS MATERIAL IS LISTED AS A CARCINOGEN BY NTP, IARC, OR OSHA.

EXPRO controls the following component(s) as potential carcinogen(s) : 2,4-Dinitrotoluene . TEL: (514) 371-5520

EXPOSURE LIMITS
TLV * (ACGIH) : None established.
PEL (OSHA) : None established.
* TLV is a registered trademark.

2,4-Dinitrotoluene:	AEL	0.5mg/M3, 8 & 12 hr TWA, Skin
	PEL (OSHA)	1.5mg/M3, Skin
	TLV (ACGIH)	1.5mg/M3, Skin

SAFETY PRECAUTIONS
Do not breathe dust. Do not get in eyes. Do not get on skin. Do not get on clothing. Wash thoroughly after handling. Wash clothing after use. Do'nt breathe burning pwdr.fumes.Keep out of reach of childn.

FIRST AID

INHALATION :
If inhaled, remove to fresh air. If not breathing, give artificial respiration, preferably mouth-to-mouth. If breathing is difficult, give oxygen. Call a physician.

SKIN CONTACT :
In case of contact, wash skin with soap and plenty of water.

EYE CONTACT :
In case of contact, immediately flush eyes with plenty of water for at least 15 minutes. Call a physician.

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FIRST AID - CONTINUED

If swallowed, induce vomiting immediately by giving two glasses of water and sticking finger down throat. Never give anything by mouth to an unconscious person. Call a physician.

NOTE: Burning smokeless powder may cause extensive and deep burns. Get medical attention immediately. Immerse burned area in cold water.

NOTE TO PHYSICIANS: Absorption of 2,4-Dinitrotoluene into the body may lead to the formation of methemoglobin that, in sufficient concentration, causes cyanosis, Since reversion of methemoglobin to hemoglobin occurs spontaneously after termination of exposure, moderate degrees of cyanosis need be treated only by supportive measures such as bed rest and oxygen inhalation. Thorough cleansing of the entire contaminated area of the body, including scalp and nails is of utmost importance. If cyanosis is severe, intravenous injection of methylene blue, one milligram per kilogram of body weight, may be of alue. Cyanocobalamin (Vitamin B12), one milligram ntramuscularly, may speed recovery. Intravenous fluids and blood transfusions may be indicated in very severe exposure.

****

PROTECTION INFORMATION

GENERALLY APPLICABLE CONTROL MEASURES and PRECAUTIONS

Use only with adequate ventilation. Keep away from heat, sparks and flames. Keep container in a cool place. Keep container tightly closed. Avoid dust generation. Do not mix with acids, alkalies.Do not consume food, drink or tobacco in areas where they may become contaminated with this material. Use sparkproof tools and equipment. Do not allow powder to accumulate in exhaust systems.

PERSONAL PROTECTIVE EQUIPMENT

Safety glasses. Protective cotton gloves.

****

SPILL, LEAK, OR RELEASE

Review FIRE AND EXPLOSION HAZARDS and SAFETY PRECAUTIONS before proceeding with clean up. Use appropriate PERSONAL PROTECTIVE EQUIPMENT during clean up.

Remove source of heat, sparks, flame, impact, friction or electricity. Pick up by hand for disposal. Do not use power equipment. Do not use imaged or wet material. Control access to area and remove sources of eat or impact. Never return to container for reuse. Use nonsparking tools tools for cleanup.

WASTE DISPOSAL

Consult an explosives manufacturer for recommended methods of destroying explosive materials. Comply with applicable Federal Regulations under

DISPOSAL INFORMATION - CONTINUED

parts 260-271). May be stored under water until disposed of.

****

SHIPPING INFORMATION

Check manufacturer or shipper for specific information.

****

.AGE CONDITIONS

Store in well ventilated area. Store in cool place. Keep container tightly closed. Do not store with other explosives.Store in accordance with National Fire Protection Assn regulations. Store in accordance with Federal Regulations. Do not store or consume food, drink, or tobacco in areas where they may become contaminated with this material. Store in approved type magazine.

****

ADDITIONAL INFORMATION AND REFERENCES

PERSONS HANDLING EXPLOSIVES MUST BE TRAINED IN THE CORRECT PROCEDURES FOR THEIR USE.

****

Date of latest Revision :
Person Responsible for MSDS : Product Manager,
Address :

Telephone :

Honeywell

Exposure of Personnel to Posttest Byproducts from a .50-Cal. Light Gas Gun

NASA JSC White Sands Test Facility

Laboratory Office

Don Henderson, HTSI

Karen Rodriguez, NASA

October 2, 2005

What Happened?

Honeywell

- In January 2002 we were talking about our holiday breaks.
  - One of the team members mentioned that he could not taste food like he used to.
  - We all agreed that we couldn't smell or taste much.
  - Another mentioned that his wife could smell the guns on him, even his car smelled.
  - In fact all of our wives had made comments about our "gun" smell.

What Happened?

- The .50-cal. gun smelled bad after shots
  - The 1-in. gun didn't smell.
  - Purges were the same for both guns.
- We were cavalier about it
  - "That's just how guns smell."
  - "Been shootin' guns for decades."
  - Typically we'd shoot, then sit down and eat lunch 10 ft away.

Investigation

Honeywell

- **First sampling on January 8, 2002 - Industrial Hygienist used MIRAN.**

Table 1

MIRAN Preliminary Results

Sample	Location	Sequence in Operation	Max. Reading for Benzene[a] (ppm)	Max. Reading for Acetaldehyde (ppm)	Max. Reading for Ammonia (ppm)
1	Breech	After gun is fired but prior to purges	13	8.3	0.7
2	High-pressure section	After gun is fired but prior to purges	4.7	6.2	6.8
3	Break area (table)	After gun is fired but prior to purges	3.9	3.8	NR[b]
4	Target chamber open	After 15 min purge, evacuation and backfill with ambient air	3.2 (outside)	11 (inside)	3.9 (outside) 2.6 (inside)
5	Expansion tank open	After 15 min purge, evacuation and backfill with ambient air	2.8 (outside) 6.4 (inside)	NR	1.4 (inside)
6	Disconnected breech from pump tube	Purged pump tube for 1 h. Gun is opened.	22	NR	NR
7	Disconnected high pressure section from pump tube	Purged pump tube for 1 h. Gun is opened.	66	NR	NR
8	Break area	After purge, gun is opened, N. high-bay door opened and fans turned on for ~ 3 min.	3	NR	NR

[a] Short Term Exposure Limit is 2.5 ppm

[b] No reading was taken with the MIRAN

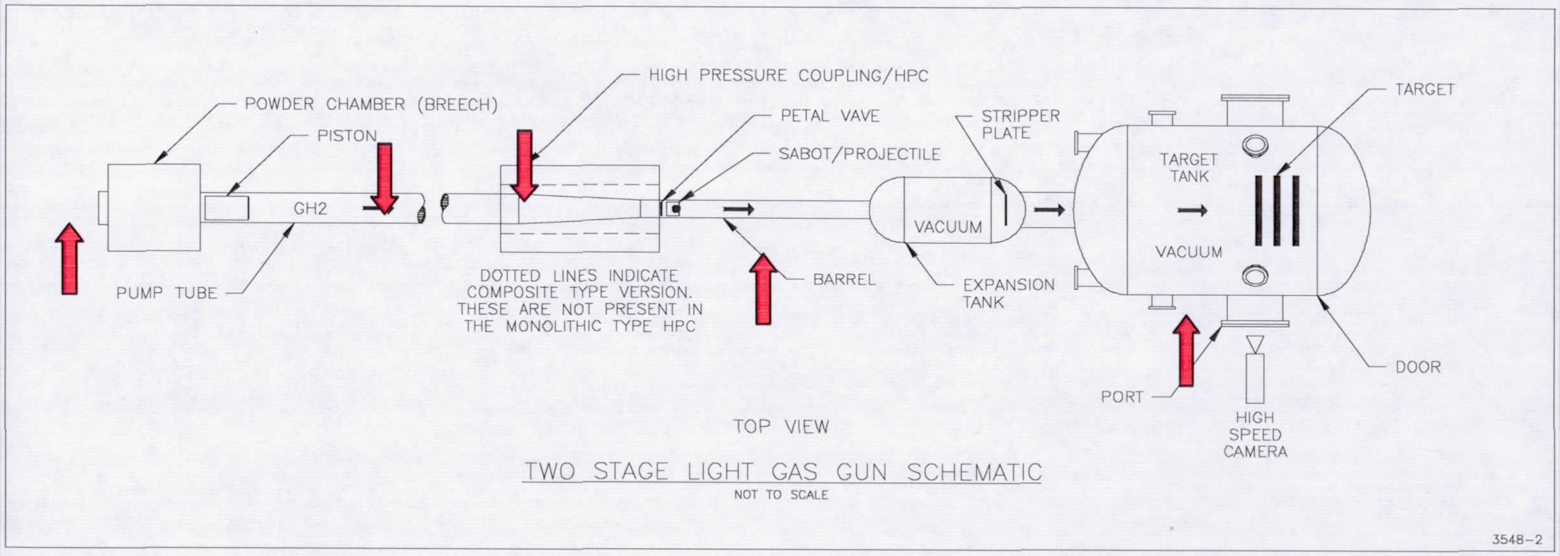
NOTES: No hydrogen cyanide was detected.

Highest level of CO detected was 1 ppm. Highest level of CO_2 detected was 644 ppm.

The MIRAN samples a spectrum and may not distinguish between specific gasses.

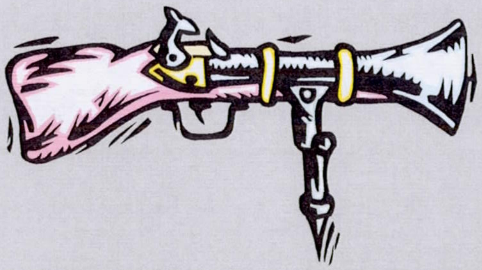
Investigation

- All testing suspended pending further investigation
- Gouges in pump tube preventing seal
- Purge lines filled with soot
- .50-cal. gun on windward side of building caused entrainment of gases into HVAC systems
  - 1-in. gun on leeward side



Investigation

- Overpressure relief devices dumped directly into the building. WSTF Chemistry/MDAL Lab performed analysis.
- January 17 - Shot .50-cal. gun with 225 grams of IMR 4198 gunpowder
  - Gathered wipe, soot and gas samples at various locations
  - SCBA, Tyvek® suits, gloves taped to suits



Wipe Sampling

Honeywell

- **Wipe Plan**

Table 2
Sampling Matrix for Hypervelocity Wipe Samples

Location	Sampled Area (ft^2)	Date
Pump tube breech	1	06 February 2002
Flight range expansion tank	1	06 February 2002
Flight range target chamber	1	06 February 2002
Blank	N/A	06 February 2002
Back of piston	0.11	06 February 2002
Breakroom table	1	18 January 2002
Rail	1	18 January 2002
Work bench	1	18 January 2002
Blank	N/A	18 January 2002

- **Wipe Results**

Table 3
Wipe Sample Results

Compound	Retention Time (min)
Pump Tube at Breech	
Octamethylcyclotetra-siloxane	5.79
Decamethylcyclopenta-siloxane	7.01
Unknown compound	8.33
2-methyl-1,3-benzenediamine	8.69
Tetradecamethylcyclohepta-siloxane	9.51
Hexadecamethylcycloocta-siloxane	10.56
Back of Piston	
Decamethylcyclopenta-siloxane	7.01
Dodecamethylcyclohexa-siloxane	8.32

Wipe Sampling

- Most notably 2-methyl-1,3-benzenediamine was found
  - Skin sensitizer and irritant
  - Not a human carcinogen, but is confirmed as an animal carcinogen

Post-shot residue on your skin can cause redness, burning, and itching. Have you felt it?

Soot Sampling

- Soot samples were collected from the pump tube and analyzed
- Results
  - Organic based compounds found in insufficient quantities to identify

NASA WSTF photo WSTF0905E07780

Pump Tube End

Air Sampling

- **Air Sample Plan**

Table 4
Sampling Matrix for .50-Cal Gun Air Samples

Location	Time & Date of Sampling	Pressure (psia ± 2%)
Baseline	0817 hrs 17 January, 2002	12.60
Breech posttest	0910 hrs 21 February, 2002	12.46
#2 High-pressure post	0915 hrs 21 February, 2002	12.56
#5 Pump tube pre-purge	0920 hrs 21 February,2002	10.81
#6 Inside target chamber	1036 hrs 21, February, 2002	12.57
#7 Inside expansion chamber	1042 hrs 21 February, 2002	12.62
#11 Breech post-purge	1124 hrs 21 February, 2002	12.65
#13 High-pressure post-purge	1113 hrs 21 February, 2002	12.63
Flight range	1045 hrs 06 February,2002	12.49
Breech	1155 hrs 22, February, 2002	12.59
High-pressure accelerator reservoir	1203 hrs 22, February, 2002	12.45

- **Air Sample Results**

Discussion

- **Possible effects on humans**
  - **Large variety of strong irritant organic compounds like aldehydes**
    - Anosmia - skin & mucous membrane burning
    - Ageusia - upper respiratory irritation
  - **Several Carcinogens**
    - Benzene - marrow suppression - A1 confirmed human
    - 1,3-Butadiene - cancer - A2 suspected human
    - Acrylonitrile - skin - A3 animal with unknown human effect
  - **Solvents**

Chemical Interaction Discussion

Honeywell

- Attempting to understand the mix best left to professionals but…
- Several modes of chemical interactions
  - Additivity - combined biological effects equal to the sum of each agent alone
  - Synergy - combined effects are greater than the sum of each agent alone
    - More serious when two or more affect the same organ or system

Chemical Interaction Discussion

Honeywell

- Solvents - like acetone, butyl acetate and methyl ethyl ketone make carcinogens more readily absorbed
  - This lowers the control limits
- It's likely that all three mixture interactions are going on in our pump tubes

Why are two-stage light gas guns worse than rifles or handguns? Relatively large amounts of gunpowder are used, and it is all contained within tubes. Rifles or handguns use much less and are typically shot out in open air or in a properly designed shooting facility. Ironically, shooting ranges are designed to limit lead exposure, but in so doing are also removing mixtures of chemicals that are arguably worse for adults.

Mitigation

Honeywell

- Purge pump tubes and flight ranges
- Route exhaust vents outside and above roof
  - vacuum pumps, purge lines, relief valves

  Vacuum pump vent
- Dump fresh air into vacuum at least four times

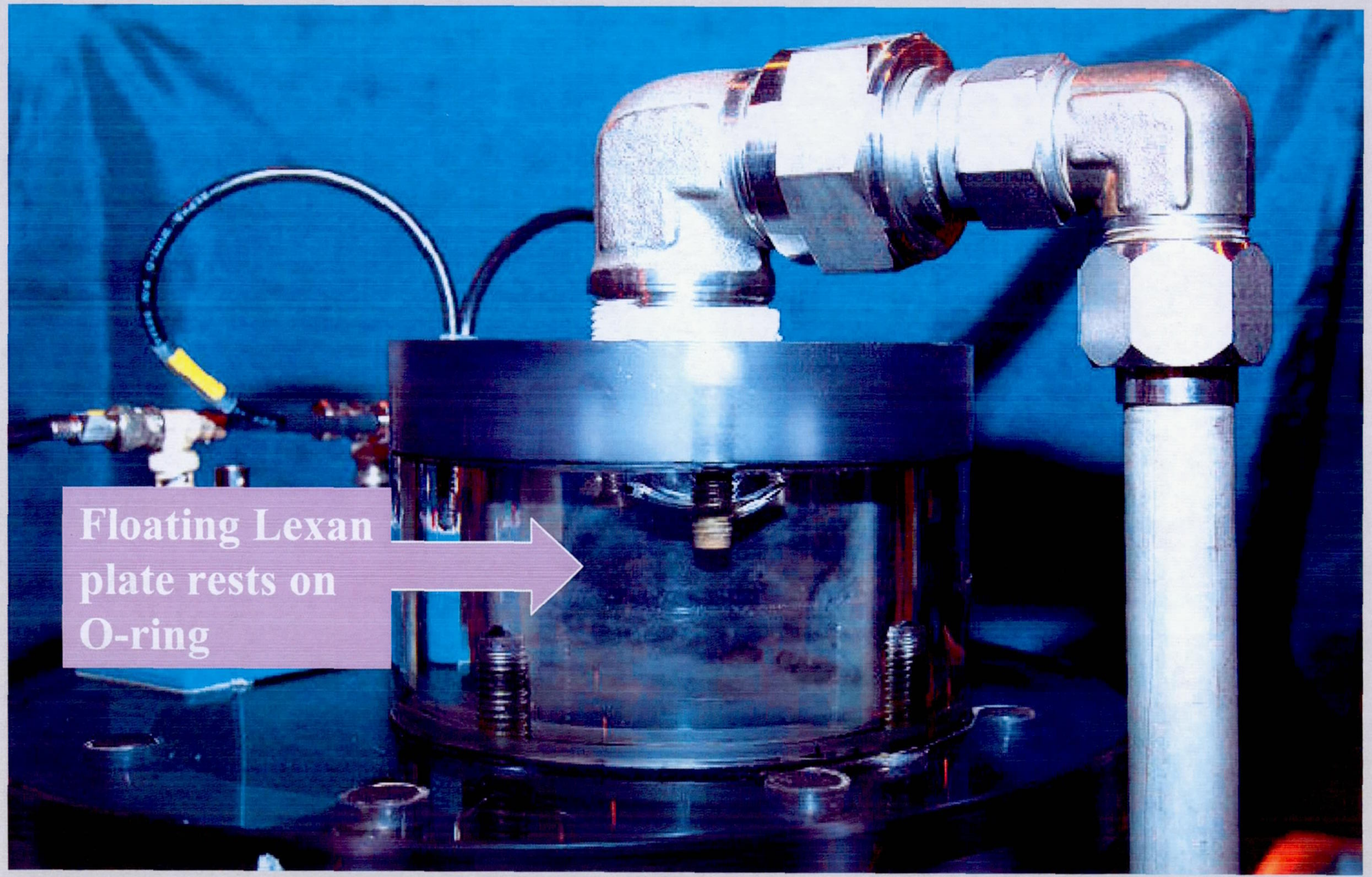
  Fresh air valve
- Exhaust fans
- Use captured relief devices

  Capture vent
- Place flow indicators on purge lines

  Flow meter

  Air tank
- Install CO detectors or real-time air monitors
- Use SCBA units or full-face respirators with GME-P100 cartridges on hand

Captured Relief Valve



NASA WSTF photo WSTF0905E07781

Ongoing Efforts

Honeywell

- **After 3.5 years we are still making improvements**
  - **Raising vent stacks higher**
    - Prevailing winds from the west. This summer, winds came from the east - exhaust in building
  - **Installing source ventilation**
    - Vehicle exhaust system over the .50-cal. Breech

Exhaust hose

Conclusions

- Sampling & analysis prove that workers can quickly be overexposed (above IDLH) to a hazardous mix of chemicals
- WSTF's analysis was performed on only 225 grams of IMR gunpowder. Larger guns will have proportionately higher levels of toxins
- Don't be tough guys, eliminate human exposure

Why did we let it happen in the first place? Admittedly, we were a bit cavalier about it. In fact, we all remember saying, "That's just how guns smell, no big deal. People have been shootin' these guns for decades." We did not know how bad the chemicals were; otherwise, we would have been more careful.

References

Honeywell

- WSTF personnel
  - Ray Gruben - Industrial Hygienist 505-524-5320
  - Karen Rodriguez/NASA - Project Manager 505-524-5279
  - Don Henderson - Project Leader 505-524-5104
- Websites
  - Occupational Safety and Health Administration (OSHA) Website, http://www.osha.gov
    - 29 CFR part 1910 Subpart Z - Toxic and Hazardous Substances
    - Table Z-1 Limits for Air Contaminants
    - Table Z-2 1910.1000 Table Z-2
  - Center for Disease Control (CDC) - National Institute for Occupational Safety and Health (NIOSH) Website, http://www.cdc.gov/niosh
    - NIOSH Pocket Guide to Chemical Hazards (NPG) - Index of Chemical Names and Synonyms
  - American Conference of Governmental Industrial Hygienists (ACGIH) Pocket Guide of TLVs and BEIs for Chemical Substances and Physical Agents and Biological Exposure Indices. www.acgih.org

NASA Johnson Space Center

White Sands Test Facility

www.wstf.nasa.gov

Honeywell

www.honeywell.com